

A Study on the Bleaching Properties of Locally Sourced Clay (Ukpor Clay) For the Processing of Palm Oil

BY

¹OLI S.C., ²KAMALU C.I.O., ^{*3}OBIJAKU J.C., ⁴OPEBIYI S.O., ⁵OGHOME
P., ⁶NKWOCHA A.C.

Department of Chemical Engineering, Federal University of Technology, Owerri, Nigeria.

ABSTRACT : *The bleaching properties of Ukpor Clay (a locally sourced clay) were studied and compared with that of imported bleaching earth for use in the bleaching of Crude Palm Oil. The effect of using the different bleaching earths on Free Fatty Acid and Peroxide value was evaluated. One factor at a time experiment was also used to determine the effect of Bleaching Temperature, Time and Adsorbent-to-Oil ratio and finally response surface methodology was used to study the effect of the three variables on bleaching on Palm Oil and determination of optimal bleaching conditions. It was observed that bleaching of Palm Oil increased the Free Fatty Acid content but reduced the Peroxide. It was also observed that FFA for the bleached palm oil reduces with increase in bleaching temperature, for both the imported bleaching earth and Ukpor clay, with the imported bleaching earth having a lower FFA value, about 1% below that of Ukpor clay, in all cases. The Bleaching efficiency increases with increase in temperature for both imported bleaching earth and Ukpor clay with the bleaching efficiencies of the imported bleaching earth and that of Ukpor clay being approximately equal at temperatures above 120OC. The bleaching efficiency also increases with increase in bleaching time or adsorbent-to-oil ratio for both imported bleaching earth and Ukpor clay. The three variables significantly affect bleaching efficiency at 95% confidence, with a good interaction among the variables. The optimum conditions for bleaching of crude palm oil using Ukpor clay are a temperature of 180OC for a time of 135mins and at an Adsorbent-to-Oil ratio of 0.05, at which it has a bleaching efficiency 80.50%. These results can be used to effectively exploit our locally sourced bleaching earth, especially in view of the contributions in this work and under the observed optimum conditions, for the processing or bleaching of palm oil.*

Key Words: Ukpor clay, imported bleaching earth, crude palm oil, bleaching properties, optimum conditions.

I. INTRODUCTION

The term bleaching refers to the treatment that is given to remove colour-producing substances and to further purify the fat or oil. Oils and fats are bleached in order to remove undesired colourants. This is because these colourants can negatively affect the taste of the oil and limit use and marketability. In addition to that, some particles or pigments that promote deterioration of oil quality, mainly due to their pro-oxidative properties that promotes oxidation, are also removed during bleaching process (Cheah and Siew, 1999). Adsorption using bleaching earths is most frequently used to remove coloured pigments in palm oil.

Ukpor clay deposit is one of the largest clay deposits in Anambra State, Nigeria, with an estimated reserve of about 12 million tones. Preliminary studies have revealed that the clay can be used for house-hold utensils. Investigations have shown that it is however possible to extend its use. This clay has high surface

activity and has shown excellent results on the bleaching of palm oil (Abane, 2000).

The study so far, in this area notwithstanding, the optimal conditions for palm oil bleaching using this local clay (adsorbent) and its comparison with imported bleaching earth is yet to be fully explored. This is the subject of this research work.

Bleaching is a process of selective removal of pigments and impurities by the physical and chemical interactions of an adsorbent with an oil or fat to improve its quality. The high cost involved in the importation of bleaching earths in the processing of palm oils necessitated the need to exploit our locally sourced bleaching earth and compare its bleaching properties with the imported bleaching earth.

The main objective of this research work is to study the bleaching of palm oil using locally sourced bleaching earth (Ukpor Clay) as raw material.

The specific objectives of this research include:

- To compare the bleaching properties of locally sourced bleaching earth with the imported bleaching earth.
- To statistically model bleaching efficiency of the locally sourced bleaching earth (Ukpor Clay) using surface response methodology.
- To determine optimal conditions for palm oil bleaching using the local bleaching earth (UkporClay).

The result of this study will increase available knowledge in the field of Palm Oil bleaching, especially using local clays like Ukpor Clay. It will provide the needed data for industries to go into large scale Palm oil bleaching using the optimum conditions so determined. Application of the findings will encourage economic boost, reduce importation and create new opportunities for use of our locally sourced clay.

The scope of this research work covers the study of palm oil bleaching using Ukpor Clay, with temperature, time and adsorbent-to-palm oil ratio as variables and its optimization using surface response methodology.

II. LITERATURE REVIEW

2.1 Bleaching Process Theory

“Bleaching” process is always being misunderstood as just a mere process of decolourization of oil & fats. In facts, “bleaching” is a process of selective removal of pigments and impurities by the physical and chemical (chemisorptions) interaction of an adsorbent with an oil or fats to improve its quality. This process refers to the art of removing not only the colour pigment, but also dirt, trace metals and various organic impurities that promote oxidation. Another term that can be used to describe bleaching process is purification process of vegetable oil.

Effective adsorption requires a large surface and practically high specific surface area. The channels by which molecules reach this surface must be negotiable by the molecules concerned. Mathematically, bleaching or purification process follows the freundlich adsorption isotherm (Howes et al, 1991).

Adsorption isotherm is the equilibrium relationships between the concentration in the fluid phase and the concentration in the adsorbent particles at a given temperature. For the cases involving liquids the

concentration is often expressed in mass units such as parts per million (PPM).

For adsorption from liquids, freundlich isotherm is applicable. Bleaching of palm oil falls under type of isotherms as the bleaching process are involving liquids (oils). The equation for freundlich isotherm for bleaching process can be illustrated as;

$$\frac{X}{M} = kC^N$$

(2.1)

Where X is quantity of substance adsorbed, M is quantity of adsorbent, C is quantity of residual substance dissolved, K and N are constants unrelated to the amounts of solute and adsorbent .

2.2 Mechanisms of Bleaching Process

During bleaching or purification, the palm oil is brought into contact with a surface- active adsorbent, and then the undesired particles or other components are selectively retained on the pore surface. Gradually, the concentration of undesired particles on the available active surface of the adsorbent and the concentration remaining in the oil come into balance, so that further exchange is negligible (Khedok and Lim, 1982).

In general, bleaching earth is a decolourising agent, which will change the tint of any coloured oil to lighter shade by changing the basic colour units in oil, without altering the chemical properties of the oil. Bleaching earths are normally used in the bleaching of palm oils. Bleaching earth works based on its character of adsorption and ion exchange. The adsorption process is influenced by some factors as follows:

- a. Particle size
- b. Adsorbent polarity
- c. Surface area
- d. Pore volume
- e. Pore size

While some of these earths are naturally bleaching, some have to be treated with mineral acids. This activation result in the replacement of some of the aluminum ions by hydrogen ions from the acid, which further results in the creation of net negative charges on the clay lattice structure and creates the cation adsorption properties of the acid-activated bleaching earths clay (Hymore, 1996).

2.3 Types of Adsorbents

There are few types of bleaching adsorbents that are being used in the manufacture of vegetable oil such

as acid activated bleaching earth, natural bleaching earth, synthetic silicates, activated carbon and synthetic resins.

a. Acid Activated Clays

These include Kaolin which contains Kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and usually oxides of iron, magnesium, calcium and alkaline metals.

Others are bentonites of other clays. Generally, they show essentially no adsorptive ability unless when activated by treatment with mineral acids, usually sulphuric acid or hydrochloric acid.

b. Natural clays

Natural bleaching clays are naturally active. They are excellent adsorbents as they are able;

i. to decrease the levels of chlorophyll and colour bodies

ii. to minimize free fatty acid increase during bleaching.

They are chiefly magnesium- Aluminum Silicates in the form of the minerals attapulgite and montmorillonites (Khedok and Lim, 1982; Lim, 1982).

The clay is heated and dried during which it develops a porous structure. It is then ground and screened.

c. Activated Carbon

It includes Carbon material mostly derived from charcoal for all three variations of the name "activated". It is sometimes substituted by "active". By any name, it is a material with an exceptionally high surface area. Just one gram of activated carbon has a surface area of approximately 500m^2 , typically determined by nitrogen gas adsorption, and includes a large amount of micro porosity. The bleaching action seems to be due to the large adsorbent surface of carbon. This large surface held in a small volume, would influence the surface tension of the compounds with which they come into contact, thus causing adsorption. There are a large number of commercial grades of activated carbon that are used for adsorbing gases and vapours, odours and colouring materials (Hamilton, 1995).

d. Synthetic Silicate

Synthetic Silicates are now commonly used in palm oil bleaching. Although synthetic silicates have a moderate capacity for pigment removal, small amounts of it are used in combination with bleaching clay.

Silica had the capability of enhancing the earth's ability to remove colour bodies, phosphorus and other minor components that affect the colour stability of the oil (Bernardini, 1988).

2.4 Types of Bleaching Methods

There are three major types of bleaching methods that can be used in edible oil industry.

1. **Heat bleaching:** some pigments such as carotenes become colourless if heated sufficiently. However this will leave pigment molecules in the oil quality. If this oil come into contact with air coloured degradation products such as Chroman-5, 6-quinones from γ -tocopherol present, may be formed. These are very difficult to remove (Ceriani and Meirelles, 2006).
2. **Chemical oxidation:** Some pigments for example carotenoids are made colourless or less coloured by oxidation. But such oxidation invariably affects the glycerides and destroys natural antioxidants. Consequently, it is never used for edible oil but restricted to oils for technical purposes such as soap-making.
3. **Adsorption:** Adsorption is the collection of a substance into the surface of an adsorbent solid. It is the common method used for bleaching edible oil. It is a removal process where certain particles are bound to an adsorbent particle surface. Bleaching agents normally possess a large surface that has a more or less specific affinity for pigment-type molecules, thus removing them from oil without damaging the oil itself.

2.5 Ukpok Clay

Ukpok clay deposit is one of the largest clay deposits in Anambra State, Nigeria, with an estimated reserve of about 12 million tones. Preliminary studies have revealed that the clay can be used for house hold utensils.

Investigation have shown that it is however possible to extend its use through a more synthetic characteristics of its properties by determining the chemical composition of the clay, its mineralogical composition and its particle size distribution. This clay has high surface activity and has shown excellent results on the bleaching of palm oil (Abane, 2000).

2.6 Properties of Natural Ukpok Clay

This clay has a chalky white colour. The clay is weak and cracks very easily. It is normally sticky except on good working conditions. The strength of the clay varies with temperature changes. As the temperature increases, the strength of the clay increases. In dry atmosphere, the clay powders are of good stability

and do not lose activity even after prolonged storage, A typical Ukpör clay has disordered kaolinite minerals hence the ultimate clay crystal carries a net negative charge. This charge results from anion adsorption into the surface or from the unbalanced lattice. The clay particle is a very complex anion (Abane, 2000).

2.7 Palm Oil

Palm oil is derived from the fleshy part or the mesocarp of the fruit of the palm species (*Elareisguineensis*).

Palm oil has a wide range of applications; about 80% are used of food applications while the rest is feed stock for a number of non-food applications. Among the food uses, bleached and refined olein is used mainly as cooking and frying oils.

Crude palm oil commonly consists of desirable triglycerides, unsaponifiable matter together with small amounts of impurities. Most of these impurities contribute undesirable effects to the oil, for instance color, flavour, odour, instability and foaming. These impurities should be removed by a purification step in order to produce good quality refined oil with minimal possible oil loss or damage to the oil.

Table 2.1: Typical Composition of Crude Palm Oil

Constituent	Crude Palm Oil
Triglycerides, %	95
Free Fatty Acid (FFA), %	2 – 5
Moisture & Impurities, %	0.15 – 3.0
Peroxide Value (PV), meq/kg	1.0 – 5.0
Diglycerides, %	2 – 6

III. RESEARCH METHODOLOGY

3.1 Materials

3.1.1 Raw Material Collection

The local clay used for the experiments was collected from Ukpör, a Town in Anambra State, Nigeria. The clay sample was collected in a well labeled nylon sack and delivered to the chemical analyst for the preliminary and main laboratory tests.

The crude palm oil was obtained from a market in Anambra State. The imported bleaching earth (Fullmonth 7000c) was made by Laporte Chemicals Warrington Cheshire, England, and was obtained from Envoy Oil Industries Ltd, Onitsha- Anambra State, Nigeria.

3.1.2 Equipment/Apparatus

Magnetic Stirring Machine, Analytical Weighing Balance (Model: Adventurer Pro A35, Make: OHAUS), Electrothermal Oven (Model: HG 9023A), (Make: B.BRANC, scientific and instrumental company, England), Electromechanical centrifuging machine (Model: D453), (Make: Searchtech), Heating mantle (Model: ZDHW-250), (Make: PEC Medical, USA), Lovibond tintometer, Viscometer (Model: HI 2211), (Make: SearchTech), Bunsen burner, Resort stand, pH Meter (Model: HI 2211), (Make: Hanna), 250ml and 500ml conical flasks, 100ml, 250ml and 500ml beakers, Measuring cylinders, 50ml volumetric flask, Separating funnels, Sieve plate, Burette, Pipettes, Specific gravity bottle, Glass funnel, Stirring rod, Spatula, Filter papers.

3.1.3 Reagents

Analytical grade Ethanol (95%), 0.1N aqueous sodium hydroxide solution, Acetic acid, Chloroform, Di-ethyl ether, Hydrochloric acid, Potassium hydroxide, Potassium iodide, Sodium thiosulfate, Starch powder, Phenolphthalein indicator solution, Distilled Water, Deionized Water.

3.2 Method

3.2.1 Preparation of Clay Sample (Ukpör)

The clay sample was oven dried at a temperature of 100°C for 24hrs. It was manually crushed to small sizes and sieved to 100 mesh.

3.2.2 Activation of Clay Sample

The clay sample was activated by the method of acid activation. 50g of sieved clay sample was mixed with 250ml of 3M HCl and heated to 105°C for 30mins.

3.2.3 Bleaching Procedure

All bleaching processes were done under atmospheric condition. The bleaching experiments were carried out in clean dry beakers containing required amount of clay and palm oil.

100ml of crude palm oil was measured into a clean dry beaker and heated at a temperature of $105 \pm 1^\circ\text{C}$. 1 gram of imported bleaching earth was added. The bleaching was carried out for 30 minutes and the mixture was stirred continuously in order to ensure complete mixing between crude palm oil and bleaching earth. After 30 minutes of contact time, the bleached oil was filtered with filter paper into another clean dry beaker. The filtrate was collected. The same procedure was repeated using locally sourced bleaching earth (Ukpör) and the amount or

percentage of pigments or particles removed was determined.

3.2.4 Determination of Amounts or Percentage of Pigments or Particles Removed Gravimetrically

Weight of palm oil = 45.5g (100ml of palm oil)

Weight of palm oil mixed with imported earth = 46.5g

Weight of palm oil mixed with local earth (Ukpor clay) = 46.5g

Weight of filtrate = 44.48g (imported bleaching earth)

Weight of filtrate (Ukpor clay) = 44.69g

For imported bleaching earth (Montmorillonite)

Mass of pigment or particles removed = wt. of palm oil – wt. of filtrate

$$= (45.5 - 44.48) \text{ g}$$

$$= 1.02 \text{ g}$$

$$\% \text{ of pigments or particles removed} = \frac{1.02 \times 100}{45.5} = 2.24\%$$

For local earth (Ukpor clay)

Mass of pigments removed = wt. of palm oil – wt. of filtrate (Ukpor)

$$= (45.5 - 44.69) \text{ g}$$

$$= 0.81 \text{ g}$$

$$\% \text{ of pigments removed} = \frac{0.81 \times 100}{45.5} = 1.78\%$$

Using specific gravity (imported earth)

Amount of pigments removed (imported earth) = specific gravity of palm oil – specific gravity of filtrate

$$\text{Amount of pigments removed} = 0.9025 - 0.8800 = 0.0225$$

$$\% \text{ of pigments removed} = 0.0225 \times 100 = 2.25\%$$

For local earth (Ukpor clay)

Amount of pigments removed = specific gravity of palm oil – specific gravity of bleached oil

$$\text{Amount of pigments removed} = 0.902 - 0.8846 = 0.0179$$

$$\% \text{ of pigments removed} = 0.0179 \times 100 = 1.79\%$$

Using 2,3 & 4 grams of imported and locally sourced earth increases the rate at which pigment or particles were removed. When the crude palm oil was heated at temperature of 150°C, refining started taking place i.e FFA began to go out.

3.2.5 Determination of the Effect of Adsorbent-to-Oil Ratio on Bleaching

Procedure: The colour value of the crude palm oil was measured using the Lovibond tintometer with a one inch cell and a value of 67.95 obtained. The bleached palm oil colour was measured using Lovibond tintometer with a one inch cell at different bleaching earth (Adsorbent) to Oil ratios of 0.0043, 0.0057, 0.0070, 0.0085 and 0.0113 for imported (montmorillonite) and locally sourced earth (Ukpor) and results were obtained. The results were used to obtain the bleaching efficiency using the colour value of the crude palm oil as base value.

3.2.6 Determination of the Effect of Bleaching Temperature on Palm Oil Colour

Procedure: The bleached palm oil colour was measured using Lovibond tintometer at different bleaching temperature of 70°C, 95°C, 110°C, 115°C, 120°C, 125°C, 127°C and 150°C for local earth (Ukpor) and imported bleaching earth (montmorillonite) and results were obtained. The results were used to obtain the bleaching efficiency.

3.2.7 Determination of the Effect of Bleaching Time on Palm Oil Colour

Procedure: The bleached palm oil colour was measured with tintometer at different bleaching time of 1hr, 2hrs, 3hrs, 4hrs, 5hrs, 6hrs, 7hrs, and results were obtained. The results were used to obtain the bleaching efficiency.

3.2.8 Response Surface Experimental Study

The experimental procedure was repeated for a response surface experimental study. A full factorial experimental design was used with the three variables; Bleaching Temperature, Bleaching Time and Adsorbent-to-Oil ratio.

The bleaching temperature is the constant temperature in degree centigrade at which the bleaching process was carried out. The bleaching time is the length of time, in minutes, that the palm oil was bleached. The adsorbent-to-oil ratio is the ratio of the amount of adsorbent used in grams, to the quantity of oil bleached in milliliters.

Table 3.1: Experimental Design Variables (Actual Values)

Variable	Lower Bound	Center Point	Upper Bound
Bleaching Temperature (°C)	70	125	180
Bleaching Time (min)	30	135	240
Adsorbent-to-Oil ratio (g/ml)	0.02	0.05	0.08

The results obtained from measurement of colour values for the twenty seven experimental runs and the computed bleaching efficiency were tabulated as presented in result table 4.15.

3.2.9 Determination of the Effect of Bleaching Temperature on Free Fatty Acid

Procedure: The free fatty acid of bleached palm oil was determined for the different palm oil samples bleached at the different bleaching temperatures of 150°C, 180°C, 200°C, 220°C, 235°C and 250°C.

Free fatty acid content of the palm oil and bleached oil was determined by titration method. 2.7g of the crude palm oil was weighed into a clean 250ml conical flask and 50ml of neutralized 95% v/v of ethanol was added. Three drops of phenolphthalein was then added and heated for about three minutes. While it is still hot, titration was carried out with 0.1N solution of NaOH and shaken vigorously to end point where the colour changes to the first permanent colour. The colour persisted for 30 seconds. The same analysis was carried out for the bleached palm oil (filtrate) using the locally sourced bleaching earth and imported bleaching earth.

For free fatty acid content of crude palm oil, the result can be expressed as:

$$FFA = \frac{25.6 \times V \times N}{W} \quad (3.1)$$

Where V is Volume of standard NaOH solution used in ml, N is normality of standard NaOH solution used and W is Weight of oil used.

For FFA content of bleached oil using imported bleaching earth and that of locally sourced (Ukpor) as 3.57% and 3.91% respectively. See Appendix A.

3.2.10 Procedure for the Peroxide Value Determination

2.10g of the crude palm oil sample was measured into a (250ml) conical flask. 30ml of acetic acid - chloroform (3:2) was added and swirled to dissolve. 1ml of saturated solution of water was added and allowed to stay in the dark for three minutes. After staying, 1ml of freshly prepared starch solution was added. If there is no colouration, it means the peroxide value is Nil, but if there is any colouration (black), the solution is titrated against 0.01N sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_4$) solution shaking vigorously to end point. Where the black colour disappears, carry out a blank test. The blank titration must not exceed 0.1ml of the 0.01N Sodium thiosulphate solution.

The peroxide is a measure of those substances in a sample expresses in terms of milli equivalent of active oxygen per kilogram which oxidize potassium iodide under conditions of test.

The result can be expressed as;

$$PV = \frac{(S-B) \times N \times 1000}{W} \quad (3.2)$$

Where S = Volume in ml of sodium thiosulphate solution of normality N used

B = Volume in ml of sodium thiosulphate solution of normality N used for the blank test

N = Normality of sodium thiosulphate solution

W = Weight in grams of the oil

Based on experiment,

S = 0.2ml

B = 0.1ml

N = 0.01

W = 2.20g

$$PV = \frac{(0.2 - 0.1) \times 0.01 \times 1000}{2.10} = 0.48 \text{ Meq/kg}$$

The peroxide value of bleached palm oil for both locally sourced earth and imported earth were Nil.

3.2.11 Atomic Absorption Spectrophotometer (AAS)

An FS 240 varian Atomic Absorption Spectrophotometer (AAS) using Nitrous oxide oxidant gas, Acetylene gas, Air oxidant gas, Distilled water, and conical flask. The Reagent used is

1000ppm Al standard solutions. The working principle of the Atomic absorption spectrometer is based on the sample being aspirated into the flame and atomized when the AAS's light beam is directed through the flame into the monochromator, and onto the detector that measures the amount of light

absorbed by the atomized element in the flame. Since metals have their own characteristic absorption wavelength, a source lamp composed of that element is used, making the method relatively free from spectral or radiational interferences. The amount of energy of the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample. The procedure involves the sample being thoroughly diluted, mixed by shaking, and 100ml of it being transferred into a glass beaker of 250ml volume. The sample is aspirated into the oxidizing air-acetylene flame or nitrous oxide acetylene flame. When the aqueous sample is aspirated, the sensitivity for 1% absorption is observed.

3.2.12 X-Ray Fluorescence (XRF)

Mini Pal is a compact Energy dispersive X-ray spectrometer designed for the elemental analysis of a wide range of samples. The system is controlled by a PC running the dedicated Mini pal analytical software. The Mini pal 4 version in use is PW 4030 X-ray Spectrometer, which is an energy dispersive microprocessor controlled analytical instrument designed for the detection and measurement of elements in a sample (solids, powders and liquids), from sodium to uranium. The sample for analysis is weighed and grounded in an agate mortar and a binder (PVC dissolved in Toulene) is added to the sample, carefully mixed, and pressed in a hydraulic press into a pellet.

The pellet is loaded in the sample chamber of the spectrometer and voltage (30KV maximum) and a current (1mA maximum) is applied to produce the X-rays to excite the sample for a preset time (10mins in this case). The spectrum from the sample is now analyzed to determine the concentration of the elements in the sample and percentage composition.

3.2.13 X-Ray Diffraction (XRD)

It is also known as x-ray diffractometer. XRD is a popular technique used for the analysis if the structural properties and the identification of minerals in solid state and material science, is needed. A brucket D 5005 power X-ray diffraction with Ni-filtered, $C_{u,K\alpha}$ -radiation was used to record diffraction spectra, prior to the measurement, each sample was prepared using a standard method for powdered sample preparation. The sample was dried in the oven at 100°C. About 1g of each sample was ground to fine powder and homogenized as much as

possible, then loaded into the poly-methyl metacrylate sample holder. The powder was gently pressed into the cavity using a glass slide, while the glass was gently lifted off to reveal the sample surface. Each diffraction spectrum recorded with condition 2 θ angle of between 5° and 50°, Cu-target, 35Kv, 35mA and scan speed of 0.3 degree/0.02 second.

Typically, the data was expressed in the plot between intensity of diffraction peaks and 2 θ angle. The positions of diffraction peaks were compared with a reference data base and the identifications of compounds calculated.

3.2.14 Fourier Transform Infra-Red (FTIR)

An FTIR-8400S Fourier Transform Infrared Spectrophotometer, made by SHIMADZU is a powerful tool for identifying types of chemical bonds (functional group) in a molecule by producing an intra-red absorption spectrum that is like a molecular "finger print".

The FTIR instrument is computerized and faster than the older dispersive instruments. The solid samples are dissolved in a methylene chloride solvent, and the solution placed onto the plate. This is called a cast film, and is frequently used for polymer identification. Solution is then analyzed in a liquid cell. This is a small container made from NaCl (or other IR-transparent material) which is filled with liquid, such as the extract for EPA 418.1 analysis. This creates a longer path for the sample, which leads to increased sensitivity. Sampling methods include making a null of a powder with hydrocarbon oil (Nujol) or pyrolyzing insoluble polymer and using the distilled pyrolyzate to cast a film.

3.2.15 Scanning Electron Microscope (SEM)

SEM is a type of microscope that uses electrons rather than light to form an image. Morphology of the solid samples could be seen through the use of SEM. Crystal shape size of the crystalline solid phase could be identified from the micrograph. The observation was done using a JOEL scanning electron microscope model JSM 6400. To prepare for the observation, the solid samples were placed on a brace stub sample holder using double stick carbon tape. Then, the samples were coated with layers of gold approximately 20-25Å thick using Blazer sputtering coater. The micrograph were recorded with 12 KV, 800x magnification.

IV. RESULTS AND DISCUSSION

4.1 Result Presentation

The results of the experiments and the instrumental analysis of the bleaching earth and palm oil samples are here-in outlined below: in tables 4.1 – 4.15 and Figures 4.1 – 4.9.

Table 4.1: Result for the FFA and Peroxide Values of Crude and Bleached Palm Oil

Parameter	Crude Palm Oil	Bleached Palm Oil using imported bleaching earth	Bleached Palm Oil using locally sourced earth (Ukpor)
Free Fatty Acid Content, FFA (%)	3.20%	3.57%	3.91%
Peroxide Value, PV (Meq/kg)	0.48	Nil	Nil

Table 4.2: Result for the AAS characterization of Ukpor Clay

Element Symbol	Al	Fe	Na	K	Mn	Ca	Ni	Mg	Cu	Zn
Concentration in Ukpor Clay (ppm)	14.35 48	16.23 06	11.50 33	0.10 76	0.22 75	0.87 70	0.09 27	0.11 35	0.01 86	0.01 79

Table 4.3: Result for the XRF analysis of Ukpor Clay

Chemical Component	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	CaO	MnO	V ₂ O ₅	Cr ₂ O ₃	ZnO	NiO	CuO	LOI
Composition in Ukpor Clay (%)	55.80	5.11	15.70	5.88	0.18	0.061	0.24	0.089	0.01	0.026	0.039	4.14

Table 4.4: Result for the FTIR spectrum of raw Ukpor Clay

Wave No (cm ⁻¹)	Peak Area (cm ⁻²)	Bond Source	Mineral
3412.39	299.07	H-O-H Stretching	Kaolinite
3109.02	346.98	O-H bending	Montmorillonite
1562.48	2.08	H-O-H bending	Kaolinite
1463.52	135.06	Si-O-Si	Quartz
1233.36	49.45	Si-O-Si Stretching	Smectite
947.69	43.80	Al-O-Si Stretching	Illite
762.13	25.92	Si-O-Al Stretching	Quartz/Illite

Table 4.5: Result for the FTIR spectrum of UHC

Wave No (cm ⁻¹)	Peak Area (cm ⁻²)	Bond Source	Mineral
3842.80	19.52	H-Al-OH Stretching	Kaolinite
3678.27	77.13	Al-O-H Stretching	Kaolinite
3614.77	5.37	Al-O-H Stretching	Illite
3455.60	9.52	Al-O-H Stretching vibration	Kaolinite
3402.24	115.01	H-Al-OH vibration	Kaolinite
3276.31	1.81	Si-O-Si	Montmorillonite
1765.65	4.86	O-H Scissoring	
1607.58	72.01	H-O-H bending	Kaolin
1184.33	51.95	Si-O stretching	Smectite
1046.88	4.09	Si-O-Al Stretching vibration	Quartz/Kaolin/

			Montmorillonite
861.22	128.37	Si-O-Al bending	Illite and Quartz
761.17	5.54	Si-O	Quartz

Table 4.6: Analysis of Variance Table

Source	Sum Square	df	Mean Square	f	Prob>f
Bleaching Temperature ($^{\circ}\text{C}$)	472.62	2	236.309	28.82	0
Bleaching Time (mins)	224.58	2	112.29	13.7	0.0002
Adsorbent-to-Oil Ratio (g/ml)	392.18	2	196.09	23.92	0
Error	163.98	20	8.199		
Total	1253.36	26			

Table 4.7: Response Surface Model Coefficients and Model Statistics

Variables	Coefficients	Std Error	T-stat	P-value	F-stat
Constant	32.9284	0.042022	783.6	3.4626e-40	SSE= 0.0042056
Temp ($^{\circ}\text{C}$)	0.4177	0.00056245	742.59	8.636e-40	DFE = 17
Time (mins)	0.1462	0.00020206	723.42	1.347e-39	DFR = 9
Ads./Oil (g/ml)	299.8844	0.82491	363.54	1.6195e-34	SSR= 1253.4
Temp*Time	-3.5772e-4	7.8622e-7	-454.99	3.5718e-36	F = 5.6293e5
Temp*Ads./Oil	1.4753	0.0027518	536.11	2.196e-37	P-VALUE = 0
Time*Ads./Oil	0.5915	0.0014414	410.39	2.063e-35	
Temp ²	-0.0014	2.1227e-6	-682.38	3.6354e-39	
Time ²	-3.9864e-4	5.8242e-7	-684.46	3.4524e-39	
Ads./Oil ²	-6.6815e3	7.1346	-936.49	1.6731e-41	
	R ² = 0.9999	Adj. R ² = 0.9998			

Table 4.8: Optimal Condition for bleaching of Ukpok Clay

Temperature ($^{\circ}\text{C}$)	Time (mins)	Adsorbent-to-Oil Ratio (g/ml)	Bleaching Efficiency (%)
154.5120	148.2246	0.0461	82.9394

Table 4.9: Result for the physico-chemical properties of imported earth (Fullmonth Clay)

Chemical Composition (%)	Standard
SiO ₂	55.00 – 65.50
Al ₂ O ₃	14.00 – 20.00
Fe ₂ O ₃	3.50 – 8.50
CaO	0.50 – 3.50
MgO	2.50 – 4.50
Na ₂ O	0.20 – 1.50
K ₂ O	0.50 – 1.50
SiO ₂	55.00 – 65.50
Al ₂ O ₃	14.00 – 20.00
Physical Properties	Standard
Loose Bulk Density (g/ml)	0.45 – 0.65
Free Moisture Content (%)	8.00 – 12.00
Acidity (% H ₂ SO ₄)	0.30 max

Source: Envoy oil industries Ltd, G.M.O Road, Nkutu, Onitsha Anambra State.

Table 4.10: Particle size distribution by sieve analysis of dry powder

Sieve size used	Range of Quantity Retained
Retained on 100 inch	0.20 – 3.00
Retained on 140 inch	3.00 – 9.00
Retained on 200 inch	10.00 – 18.00

Table 4.11: Effect of bleaching temperature on bleaching efficiency

Temp. (°C)	Colour Value (Imported)	Colour Value (Ukpor)	Bleaching Efficiency (%), (Imported)	Bleaching Efficiency (%), (Ukpor)
70	25.0	26.0	63.2082	61.7366
95	24.0	25.2	64.6799	62.9139
110	23.2	24.8	65.8572	63.5026
115	23.0	23.5	66.1516	65.4157
120	22.0	22.0	67.6233	67.6233
125	20.0	21.4	70.5666	68.5063
127	19.4	19.5	71.4496	71.3024
150	18.0	18.0	73.5099	73.5099

Table 4.12: Effect of bleaching time on bleaching efficiency

Time (hrs)	Colour Value (Imported)	Colour Value (Ukpor)	Bleaching Efficiency (%), (Imported)	Bleaching Efficiency (%), (Ukpor)
1	26.00	26.00	61.7366	61.7366
2	25.20	25.50	62.9139	62.4724
3	24.01	24.80	64.6652	63.5026
4	23.10	23.50	66.0044	65.4157
5	22.00	22.10	67.6233	67.4761
6	21.50	21.80	68.3591	67.9176
7	21.00	20.10	69.0949	70.4194

Table 4.13: Effect of bleaching adsorbent-to oil ratio on bleaching efficiency

Adsorbent-to-Oil Ratio (g/ml)	Colour Value (Imported)	Colour Value (Ukpor)	Bleaching Efficiency (%), (Imported)	Bleaching Efficiency (%), (Ukpor)
0.0043	13.00	14.10	80.8683	79.2494
0.0057	12.04	13.10	82.2811	80.7211
0.0070	11.10	12.05	83.6645	82.2664
0.0085	10.50	11.20	84.5475	83.5173
0.0113	9.20	10.00	86.4606	85.2833

Table 4.14: Effect of bleaching temperature on FFA

Temperature (°C)	150	180	200	220	235	250
FFA of Bleached Oil (Imported)	9.50	8.01	6.00	5.00	4.10	3.50
FFA of Bleached Oil (Ukpor)	9.80	8.50	6.90	5.60	4.80	4.00

Table 4.15: Response Surface Experimental Result

Bleaching Temp (°C)	Bleaching Time (mins)	Adsorbent-to-oil Ratio (g/ml)	Colour Value	Bleaching Efficiency (%)
70	30	0.02	24.40	64.09

70	30	0.05	25.35	62.69
70	30	0.08	34.50	49.23
70	135	0.02	19.60	71.16
70	135	0.05	19.30	71.60
70	135	0.08	27.15	60.04
70	240	0.02	20.80	69.39
70	240	0.05	19.20	71.74
70	240	0.08	25.80	62.03
125	30	0.02	18.65	72.55
125	30	0.05	17.95	73.58
125	30	0.08	25.40	62.62
125	135	0.02	15.25	77.56
125	135	0.05	13.30	80.43
125	135	0.08	19.50	71.30
125	240	0.02	17.85	73.73
125	240	0.05	14.60	78.51
125	240	0.08	19.55	71.23
180	30	0.02	18.85	72.26
180	30	0.05	16.50	75.72
180	30	0.08	22.30	67.18
180	135	0.02	16.85	75.20
180	135	0.05	13.25	80.50
180	135	0.08	17.80	73.80
180	240	0.02	20.85	69.32
180	240	0.05	15.95	76.53
180	240	0.08	19.25	71.67

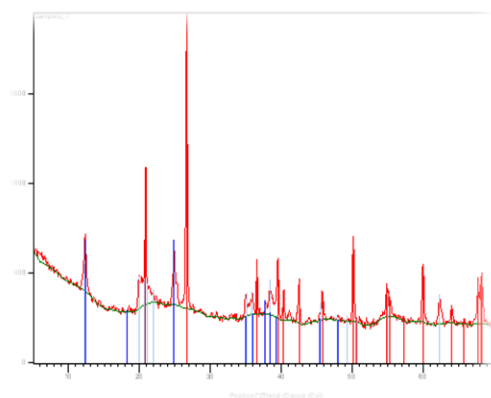


Figure 4.1: XRD Spectrum of Ukpore Clay

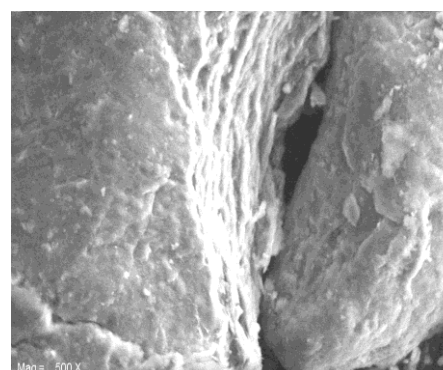


Figure 4.2: SEM analysis of Ukpore Clay at 20microns particle size

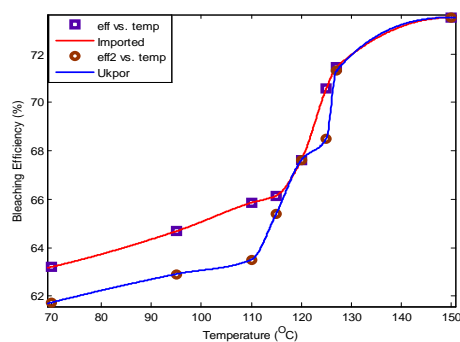


Figure 4.3: Effect of Bleaching Temperature on Bleaching Efficiency

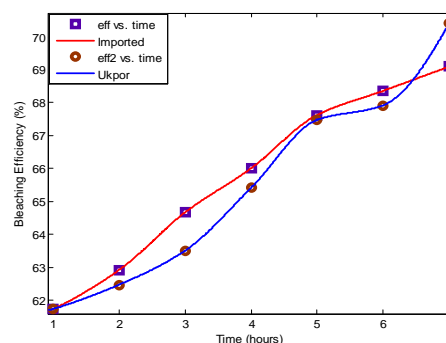


Figure 4.4: Effect of Bleaching Time on Bleaching Efficiency

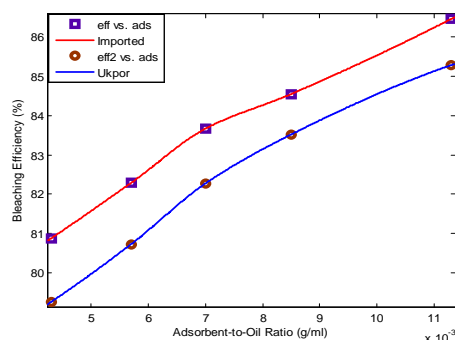


Figure 4.5: Effect of Adsorbent-to-Oil Ratio on Bleaching Efficiency

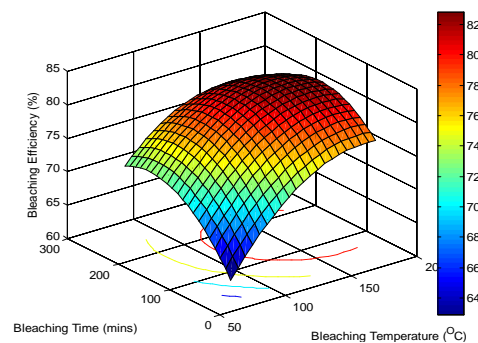


Figure 4.6: Surface Plot of Bleaching Temp. and Time vs. Bleaching Efficiency

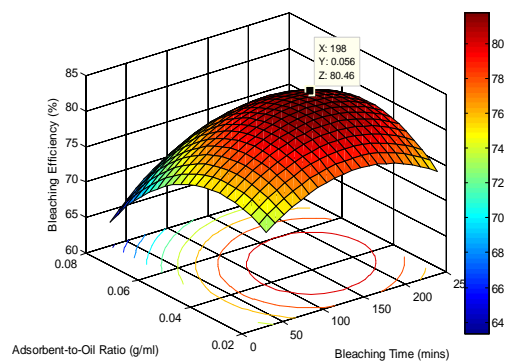


Figure 4.7: Surface Plot of Bleaching Time and Adsorbent-to-Oil Ratio vs. Efficiency

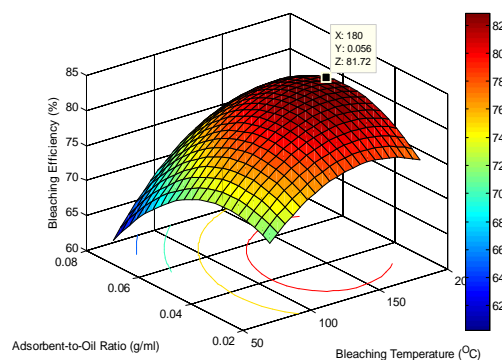


Figure 4.8: Surface Plot of Bleaching Temp. and Adsorbent-to-Oil Ratio vs. Efficiency

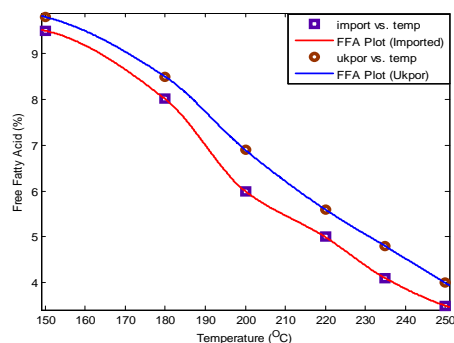


Figure 4.9: Plot of Free Fatty Acid versus Bleaching Temperature

4.2 Discussion

From table 4.1, the crude palm oil before bleaching was effected gave a free fatty acid value of 3.20%. This value increased after adsorption and bleaching had occurred. This is expected due to the acidity of the adsorbent (bleaching earth) and due to splitting or hydrolysis of palm oil triglyceride by heating. FFA is formed when the bound fatty acids in palm oil triglyceride are split either by chemical or enzymatic hydrolysis. The imported bleaching earth gave FFA of 3.57% while the locally sourced earth was 3.91% showing a slight difference of 0.34%. It indicates that the locally sourced bleaching earth compares favourably with the imported bleaching earth.

Again from table 4.1, the peroxide value of crude palm oil was 0.48Meq/kg. This value shows that its peroxide value is acceptable and the oil sample is of good quality. The peroxide value for the bleached palm oil was Nil. It indicates that there was no colouration (no black colour).

Figure 4.9 shows the effect of bleaching temperature on Free Fatty Acid (FFA). It can be observed that FFA for the bleached palm oil reduces with increase in bleaching temperature, for both the imported bleaching earth and Ukpore clay, with the imported bleaching earth having a lower FFA value, about 1% below that of Ukpore clay, in all cases.

It can be observed from the plot on Figure 4.3 that Bleaching efficiency increases with increase in temperature for both imported bleaching earth and Ukpore clay. The rate of increase of the bleaching efficiency with increase in temperature is low at low temperatures ($70 - 120^{\circ}\text{C}$) for the imported bleaching earth and Ukpore clay, but it is high beyond 120°C . The Bleaching efficiency of the Imported bleaching earth is higher than that of Ukpore clay at low temperatures by a margin of about 2%, but beyond 120°C (especially from 130°C) the bleaching efficiencies of the imported bleaching earth and that of Ukpore clay are approximately equal.

It can be observed from Figure 4.4 that the bleaching efficiency also increases with increase in bleaching time for both imported bleaching earth and Ukpore clay. The bleaching efficiency is about the same for the two samples for bleaching times of 1hour and 6.4hours, but between 1hour and 6.4hours, the imported bleaching earth has greater bleaching efficiency than Ukpore clay, while, beyond 6.4hours bleaching time, Ukpore clays gives a bleaching efficiency above that of the imported bleaching earth. The maximum margin by which the imported

bleaching earth exceeds Ukpore clay in bleaching efficiency for bleaching times between 1hour and 6.4 hours is 1.5%.

It can be observed from Figure 4.5 that the bleaching efficiency also increases with increase in the ratio of adsorbent to crude palm oil used (dosage). This increase is almost linear, having approximately the same rate. The imported bleaching earth has a higher bleaching efficiency as the adsorbent-to-oil ratio is increased. It is consistently about 1% above Ukpore clay in the observed bleaching efficiencies for all adsorbent-to-oil ratios studied.

Table 4.6 contains the result for the analysis of variance. The results reveal that the three variables; Bleaching Temperature, Bleaching Time and Adsorbent-to-Oil ratio, are all significant in bleaching efficiency at 95% confidence, since they all have p-value less than 0.05, with Bleaching Temperature and Adsorbent-to-Oil ratio being the most significant in the study.

Table 4.7 contains results for model fit, accuracy and adequacy. The F-statistics shows that the model is adequate, based on a p-value of zero, and the model accuracy can be observed from the coefficient of determination (R^2) which reveals that the model explains more than 99% of the variability observed in the experimental data. All coefficients and thus variables (main effects and interactions) are significant. This can be observed from the p-values, which is less than 0.05 for all variables, thus indicating a high level of interaction among all parameters.

The surface plots (Figure 4.6, Figure 4.7 and Figure 4.8) reveal increase in bleaching efficiency with increase in all three variables, with a good interaction among the variables. The contour lines also indicate the presence of a global optimum (maximum) value for the bleaching efficiency.

Table 4.8 gives the results of the response surface optimization, indicating that the optimum conditions for bleaching of crude palm oil using Ukpore clay are a temperature of 154.5120°C for a time of 148.2246mins and at an Adsorbent-to-Oil ratio of 0.0461.

The AAS result is presented in Table 4.2. It shows the concentration of different elements that are present in the clay samples. From the result, it is observed that the major elements in Ukpore clay are alumina, iron and sodium while traces of elements such as potassium, manganese, calcium, nickel were

also observed. The biggest element in terms of composition in Ukpok clay was iron.

X-ray Fluorescence (XRF) was performed to determine the chemical compositions of the minerals that are present in the clay. The results of the chemical analysis are presented in Table 4.3. It is seen that the clay gave a high silica oxide content (up to 56%) which indicates that they can be used as a source of silica for the production of floor tiles (Nwabanne and Ekwu, 2013). The other major oxides in the clay are Ferrous oxide and Alumina oxide though in varying compositions. There were also traces of other oxides such as calcium, zinc, nickel and copper among others in very small quantities. Ajemba and Onukwuli (2012) got similar results of chemical composition.

The X-ray diffraction shown in Figures 4.1 and 4.2 showed the various phases of the clay samples providing information on unit cell dimensions. The mineralogical phases of the clay sample showed that it consists of Fe_2O_3 , Ni_2SiO_4 (liebenbergite), $\alpha\text{-SiO}_2$ (alpha silicon), $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (nacrte), $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (Kaolinite). The graph of Ukpok clay has many peaks showing that it is crystalline. The crystallinity property was also observed during the grinding operation of the clays. The peaks show the dominant mineral phases in Ukpok clay. Preeti and Singh (2007) got similar mineral compositions using clay from Katni district of Madhya Pradesh.

The chemical structure of the adsorbent is of vital importance in understanding the adsorption process. The FTIR technique is an important tool to identify the characteristic functional groups, which are instrumental in adsorption of aromatic compounds. FTIR studies of these adsorbents helps in the identification of various forms of the minerals present in the clay. The coupled vibrations are appreciable due to the availability of various constituents (Preeti and Singh, 2007).

The results of the FTIR are shown in Tables 4.4. It is seen that there were strongly structural modification on the clay samples that were activated by the acid which is different from the raw clays as can be seen from the figures.

The Ukpok clay showed much changes in the transmission level of their peak values (about 2.0).

The maximum adsorption band increases after activation for Ukpok clay. The activated clays brought out many adsorption bands that could not be observed in the natural clay especially in Ukpok clay.

The wave numbers 3410, 3520, and 1600 correspond to H-O-H stretching while those of 3270, 1386, 1320, and 1230 corresponds to Si-O-Si stretching and 3678, 3680, and 950 correspond to Al-O-H stretching. The results of these FTIR analyses confirm the presence of some minerals such as Kaolinite and Montmorillonite. Hence, the Ukpok clay is mainly Kaolinite and Montmorillonite. Ajemba and Onukwuli (2012) equally got similar results of the bond source.

Tables 4.3 show the result of SEM analysis. SEM analysis is used to show the morphology or texture, crystalline structure and surface topography of the adsorbent. The SEM analysis of some clays indicates coarse and loosely packs with some well-formed flakes and irregular and hexagonal edges (Kaolinites). Others may appear as plates of variable thickness and size with relatively well defined edges (Illites) or showing some elements of curling layers in the particles (Smectite) (Bajwa, 2002). Chlorites appeared as inter-relating platy particles with well-defined sub-angular borders. Vermiculite manifested that the reference clay micrographs in the form of aggregate of very small particles with curled edges. Although the preliminary study suggested that clay minerals could be characterized and identified by exploiting their morphological features (using as many as possible clay minerals as standards to cover a range of morphological features). The result showed that Ukpok clay was loosely packed. In terms of coarseness, Ukpok clay showed to be verycoarsed.

The response surface model equation can be given as:
 Bleaching Efficiency = $32.9284 + 0.4177 \cdot \text{Temp} + 0.1462 \cdot \text{Time} + 299.8844 \cdot \text{Ads./Oil} - 3.5772 \cdot 10^{-4} \cdot \text{Temp} \cdot \text{Time} + 1.4753 \cdot \text{Temp} \cdot \text{Ads./Oil} + 0.5915 \cdot \text{Time} \cdot \text{Ads./Oil} - 0.0014 \cdot \text{Temp}^2 - 3.9864 \cdot 10^{-4} \cdot \text{Time}^2 - 6.6815 \cdot 10^{-3} \cdot \text{Ads./Oil}^2$

The response surface model obtained above was used to run a MATLAB 7.9 optimization code to obtain the bleaching temperature, bleaching time and adsorbent-to-oil ratio that give the maximum bleaching efficiency. The results obtained and the optimum bleaching efficiency predicted by the response surface model are given in Table 4.8.

V. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Imported bleaching earth only out performs the locally sourced bleaching earth (Ukpok clay) in terms

of its bleaching ability by a very small margin which is out stripped at high temperatures and for longer bleaching times. The optimum value of bleaching efficiency predicted by the response surface model (82.9394%) is well beyond the range of 75-80% given in literature as bleaching efficiency observed for some imported bleaching earths.

This research has helped broaden understanding on the suitability of a locally sourced clay (from Ukpok, Anambra State of Nigeria) for use in the bleaching of palm oil. As a matter of fact, the findings have revealed that the Ukpok clay compare adequately with the imported bleaching earth, hence helping broaden knowledge and understanding in the possible substitution of imported bleaching earth with our local clay in the palm oil processing industry.

5.2 Recommendation

It is imperative to exploit our locally sourced bleaching earth, especially in view of the contributions in this work and under the observed optimum conditions, for the processing or bleaching of palm oil. It is cost effective and based on the experimental data analysis done; its performance can be compared favourably with the imported bleaching earth. In fact, it can serve as a substitute for imported earth in the processing of palm oil.

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APPENDIX A

Calculation of Free Fatty Acid Contents:

For Free Fatty Acid Content of Bleached Oil using Imported Bleaching Earth

The result can be expressed as:

$$FFA = \frac{25.6 \times V \times N}{W}$$

Based on experimental,

$$W = 2.60\text{g}$$

$$N = 0.098$$

$$V = 3.7\text{ml}$$

$$FFA = \frac{25.6 \times 3.7 \times 0.098}{2.60} = 3.57\%$$

Free Fatty Acid of bleached oil using imported earth = 3.57%

For Free Fatty Acid Content of Bleached Oil using Locally Sourced Bleaching Earth (Ukpor)

The result can also be expressed as:

$$FFA = \frac{25.6 \times V \times N}{W}$$

Based on experiment,

$$W = 2.50\text{g}$$

$$N = 0.098$$

$$V = 3.9\text{ml}$$

$$FFA = \frac{25.6 \times 3.9 \times 0.098}{2.50} = 3.91\%$$

Free fatty acid of bleached oil using local earth = 3.91%